

PATENT SPECIFICATION

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COMPLETE SPECIFICATION

Substituted Benzoylacetanilides

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we

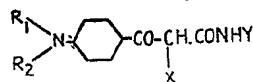
5 pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to new colour couplers for colour photography.

15 The colour couplers conventionally used in colour photography for the formation of the yellow image give azomethine dyestuffs with two main disadvantages. Firstly the dyestuffs are fugitive to light, especially the ultra-violet light present in normal daylight, so that the yellow colour image fades on exposure to normal daylight, and secondly the dyestuffs have some undesired absorption in the green region of the spectrum.

20 We have now found that certain substituted benzoylacetanilides as hereinafter defined, have a very low absorption in the green region of the spectrum and have a marked absorption in the ultra-violet so that the excess unreacted colour coupler left in the photographic layer after colour development serves to absorb ultra-violet light and thereby largely protects the yellow azomethine dyestuff image from fading.

25 According to our invention we provide new colour couplers of the formula:—



30 wherein R_1 and R_2 are alkyl, aralkyl, aryl or cycloalkyl radicals, which can be the same or different or R_1 and R_2 are joined together to form with the nitrogen atom a heterocyclic ring, Y is an aryl radical and X is a hydrogen or a chlorine atom.

[Price 3s. 6d.]

The alkyl, aralkyl, aryl or cycloalkyl radicals represented by R_1 and R_2 may be substituted with for example halogen such as chlorine or bromine, alkyl groups such as methyl, ethyl, butyl, dodecyl, or octadecyl or alkoxy groups such as methoxy, or ethoxy. The aryl radical represented by Y may be substituted with for example amino or substituted amino groups such as N-methyl-N-octadecylamino, acid groups such as carboxylic or sulphonic acid groups, nitro groups, alkyl groups such as methyl, alkoxy groups such as methoxy, trifluoromethyl groups, halogen atoms such as chlorine, or acylamino groups such as acetyl-amino.

40 According to a further feature of our invention we provide a process for the manufacture of new colour couplers which do not contain an amino group in the aryl radical represented by Y which comprises heating an aromatic amine of the formula YNH_2 with an ester of

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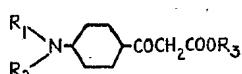
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wherein R_1 , R_2 and Y have the significance given above and R_3 is an alkyl radical, and subsequently replacing a hydrogen atom of the CH_2 group by chlorine if desired by treatment with phosphorous pentachloride.

The radical R_3 may be for example methyl or ethyl.

The process of our invention may be conveniently carried out by heating the reagents together in a solvent which is inert under the conditions of the reaction for example xylene, chlorobenzene or pyridine, and the product may be isolated by distilling off some or all of the solvent, cooling and filtering.

Price 4s 6d.

Price 75p

Price 33p

The esters used in the process of our invention may be made by condensing the appropriate *p*-disubstituted-aminobenzoyl chloride with alkyl acetoacetate and sodium alkoxide or with the sodium alkyl acetoacetate, and hydrolysing the *p*-disubstituted-aminobenzoyl-acetoacetic ester so formed to the corresponding alkyl *p*-disubstituted-aminobenzoyl-acetate. The *p*-disubstituted aminobenzoyl chloride may be made from the appropriate N:N-disubstituted aniline by treating it with phosgene, hydrolysing with caustic soda and separation of the carboxylic acid and then treating the carboxylic acid with thionyl chloride.

As examples of suitable esters for use in the process of our invention there may be mentioned ethyl or methyl *p*-dimethylaminobenzoylacetate, ethyl *p*-N-ethyl-N-benzylaminobenzoylacetate, ethyl *p*-piperidino-benzoylacetate, ethyl *p*-N-ethyl-N-cyclohexylbenzoylacetate or ethyl *p*-N-methyl-N-phenylaminobenzoylacetate, and as example of suitable aromatic amines there may be mentioned 3-amino-4-N-methyl-N-octadecylaminobenzoic acid, sulphamic acid, 3-amino-4-N-methyl-N-octadecylamino-benzene sulphonic acid, 5-diethylsulphamyl-2-methoxy-aniline, 3-amino-4-chloro-benzotri fluoride, 2:5-dimethoxyaniline, 4-amino-4¹-chloro-diphenyl ether, *o*-toluidine, *p*-nitroaniline, *o*-amino-N:N-dimethylaniline or aniline.

According to a further feature of our invention we provide a process for the manufacture of those new colour couplers which contain an amino group in the aryl radical represented by Y, which comprises treating a new colour coupler, as hereinbefore defined, containing a nitro group in the aryl radical represented by Y with a reducing agent.

This process of the invention may be conveniently carried out by treating a solution of the nitro compound in a solvent, for example water or acetic acid, with a reducing agent, for example iron, and the amino compound so obtained may be isolated by filtering, distilling off some or all of the solvent, cooling and filtering.

According to a further feature of our invention we provide a modified process for the manufacture of those new colour couplers which contain an acylamino group in the aryl radical represented by Y which comprises treating a new colour coupler, as hereinbefore defined, containing an amino group in the aryl radical represented by Y with an acylating agent.

This process of the invention may be conveniently carried out by treating a solution of the amino compound in a solvent, for example acetic acid, with an acylating agent for example octadecenylsuccinic anhydride and isolating the product from the reaction mixture.

The new colour couplers of our invention

may be used in the developing solution or they may be included in a light-sensitive layer or in a non-light sensitive layer adjacent to a sensitive layer or separated therefrom by a water-permeable colloid layer.

It is a preferred feature of our invention, however, to include the new colour couplers of our invention in a light-sensitive gelatino-silver halide emulsion layer which forms part of a multilayer film or paper of the kind used for colour photography. For this purpose it is preferred to use those new colour couplers which contain a solubilising group and a substituent rendering them fast to diffusion, for example an alkyl chain containing at least 16 carbon atoms.

The multilayer film may be a natural order negative in which the images are to be formed in colours complementary to the sensitivities of the layers or one in which an unnatural order is used, for example, one in which in the top layer there is formed a yellow image of the blue parts of the object, in one of the two lower layers there is formed a cyan image of the green parts of the object and the other, a magenta image of the red parts of the object.

The invention is illustrated but not limited by the following Examples in which the parts are by weight.

EXAMPLE 1.

11 parts of 3-amino-4-(N-methyl-N-octadecylamino)benzoic acid are dissolved in 70 parts of chlorobenzene and the solution is stirred and heated to 130° C. A solution of 6.4 parts of ethyl *p*-dimethylaminobenzoylacetate in 20 parts of chlorobenzene and 1 part of pyridine is added during 20 minutes. The solution is then heated and 27 parts of a mixture of ethanol and chlorobenzene are distilled off during 30 minutes. The mixture is boiled under a reflux condenser for 2 hours and a further 20 parts of chlorobenzene are then distilled off during 30 minutes. The reaction mixture is cooled and the anilide which crystallises out is filtered off, washed with 130 parts of boiling ethanol, and recrystallised from 175 parts of *n*-butanol. *p*-Dimethylaminobenzoylacet-(2-N-methyl-N-octadecylamino-5-carboxy)anilide is obtained in the form of white needle-shaped crystals which melt at 159—161° C. On analysis the product is found to contain 73.1% of carbon, 9.2% of hydrogen and 7.1% of nitrogen. (Calculated for C₃₁H₅₁O₄N₃ Carbon = 73.2%; Hydrogen = 9.4%; Nitrogen = 6.9%).

The ethyl *p*-dimethylaminobenzoylacetate used in the above Example may be prepared by reacting *p*-dimethylaminobenzoyl chloride with ethyl acetate and sodium ethoxide by the general method described by Claisen (Annalen 1896, Volume 291, page 65) and hydrolysing the *p*-dimethylaminobenzoyl-acetoacetic ester so formed with an aqueous solution of ammonia and ammonium chloride at 35—40° C.

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EXAMPLE 2.

In place of the 6.4 parts of ethyl *p*-dimethylaminobenzoylacetate used in the above Example there are used 8.8 parts of ethyl *p*-N-benzyl-N-ethyl-aminobenzoylacetate. The *p*-N-benzyl-N-ethyl-aminobenzoylacet - (2-N-methyl-N-octadecylamino-5-carboxy)anilide forms white needle-shaped crystals which melt at 125-127° C. On analysis the product is found to contain 75.3% of carbon, 9.0% of hydrogen and 6.0% of nitrogen. (Calculated for $C_{44}H_{68}O_4N_3$ Carbon = 75.9%; Hydrogen = 9.0%; Nitrogen = 6.0%).

The ethyl *p*-N-benzyl-N-ethylaminobenzoylacetate used in the above Example may be obtained by reacting *p*-N-benzyl-N-ethylaminobenzoylchloride with ethyl acetoacetate and sodium ethoxide by the general method described by Claisen (Annalen 1896, Volume 291 at page 65) and hydrolysing the *p*-N-benzyl-N-ethylaminobenzoylacetate ester so formed with an aqueous solution of ammonia and ammonium chloride at 35-40° C.

The *p*-N-benzyl-N-ethylaminobenzoylchloride may be obtained by treating with thionyl chloride a toluene solution of *p*-N-benzyl-N-ethylaminobenzoic acid which may be obtained by reacting *N*-benzyl-N-ethylaminobenzene with phosgene and subsequently with sodium hydroxide.

EXAMPLE 3.

In place of the 11 parts of 3-amino-4-N-methyl-N-octadecylaminobenzoic acid used in Example 1, there are used 10.6 parts of 3-amino-4-N-methyl-N-hexadecylaminobenzoic acid. *p*-Dimethylaminobenzoylacet - (2-N-methyl-N-hexadecylamino-5-carboxy)anilide is obtained in the form of white needle-shaped crystals which melt at 164-6° C. On analysis the product is found to contain 72.2% of carbon, 9.1% of hydrogen and 7.2% of nitrogen. (Calculated for $C_{35}H_{53}O_4N_3$ Carbon = 72.7%; Hydrogen = 9.2%; Nitrogen = 7.3%).

EXAMPLE 4.

3.76 Parts of ethyl *p*-dimethylaminobenzoylacetate and 2.8 parts of 3-amino-4-dimethylaminobenzoic acid are dissolved in 20 parts of pyridine. The solution is boiled under a reflux condenser for 1½ hours and 15 parts of pyridine are then distilled off. The residue is cooled and added to 150 parts of ether. The solid which separates out is filtered off, washed with ether and dried. Crystallisation of the solid from dioxane gives *p*-dimethylaminobenzoylacet - (2-dimethylamino-5-carboxy)anilide, in the form of white needles which melt at 195-6° C. On analysis the product is found to contain 65.0% of carbon, 6.4% of hydrogen and 11.8% of nitrogen. (Calculated for $C_{20}H_{23}O_4N_3$ Carbon = 65.1%; Hydrogen = 6.2%; Nitrogen = 11.4%).

EXAMPLE 5.

In place of the 11 parts of 3-amino-4-N-methyl-N-octadecylaminobenzoic acid used in Example 1 there are used 6.7 parts of 5-diethylsulphamyl-2-methoxyaniline. The reaction mixture is cooled and added to a mixture of benzene and a petroleum ether (which has a boiling point of 60-80° C.). The solid which separates out is filtered off and dried. *p*-Dimethylaminobenzoylacet - (5-diethylsulphamyl-2-methoxy) anilide crystallises from a mixture of benzene and a petroleum ether (which has a boiling point of 60-80° C.) in the form of white needles which melt at 135-137° C. On analysis the product is found to contain 59.1% of carbon, 6.5% of hydrogen and 9.2% of nitrogen. (Calculated for $C_{22}H_{22}O_5N_3S$ Carbon = 59.1%; Hydrogen = 6.5%; Nitrogen = 9.4%).

EXAMPLE 6.

In place of the 6.7 parts of 5-diethylsulphamyl-2-methoxyaniline used in Example 5 there are used 5.2 parts of 2-chloro-5-trifluoromethylaniline. *p*-Dimethylaminobenzoylacet - (2-chloro-5-trifluoromethyl)anilide crystallises from methanol in the form of featherly white needles, which melt at 193-5° C. On analysis the product is found to contain 7.0% of nitrogen. (Calculated for $C_{18}H_{16}O_2N_2F_3Cl$, Nitrogen = 6.9%).

EXAMPLE 7.

In place of the 6.7 parts of 5-diethylsulphamyl-2-methoxyaniline used in Example 5 there are used 4.1 parts of 2:5-dimethoxyaniline.

p-Dimethylaminobenzoylacet - (2:5-dimethoxy)anilide crystallises from methanol in the form of white needles, which melt at 143-5° C. On analysis the product is found to contain 66.7% of carbon, 6.4% of hydrogen and 8.2% of nitrogen. (Calculated for $C_{19}H_{22}O_4N_2$ Carbon = 66.7%; Hydrogen = 6.4%; Nitrogen = 8.2%).

EXAMPLE 8.

In place of the 6.7 parts of 5-diethylsulphamyl-2-methoxyaniline used in Example 5 there are used 5.9 parts of *p*-(4¹-chlorophenoxy)aniline. *p*-Dimethylaminobenzoylacet-(4¹-[4¹-chlorophenoxy]-)anilide crystallises from ethylacetate in the form of white needles, which melt at 180-3° C.

EXAMPLE 9.

In place of the 2.8 parts of 3-amino-4-dimethylaminobenzoic acid used in Example 4 there are used 1.67 parts of *o*-toluidine. *p*-Dimethylaminobenzoylacet-*o*-toluidide crystallises from methanol in the form of white needles which melt at 158-160° C.

EXAMPLE 10.

5.1 parts of sulphanilic acid are stirred in

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50 parts of pyridine and the mixture is heated at 110° C. 3.04 parts of triethylamine are added during 10 minutes and the mixture is then heated to 160° C. when a clear solution is obtained. A solution of 7.2 parts of ethyl-*p*-dimethylaminobenzoyl acetate in 10 parts of pyridine is then added and 10 parts of pyridine distilled off during 30 minutes. The mixture is boiled under a reflux condenser for 2½ hours and the solvent is then distilled off.

The residual oil is stirred with water and a 10% aqueous solution of hydrochloric acid is added until the mixture has a pH of 4. The solid so obtained is filtered off, washed with water and dried. The solid is then stirred with 100 parts of ether, the solid filtered off and dried. *p*-Dimethylaminobenzoylacetanilide - 4-sulphonic acid crystallises from aqueous ethanol in the form of a pale buff microcrystalline solid which decomposes without melting at 220—223° C. On analysis the product is found to contain 54.4% of carbon, 5.0% of hydrogen, 7.6% of nitrogen and 9.1% of sulphur. (Calculated for $C_{17}H_{18}O_5N_2S$ Carbon = 56.4%; Hydrogen = 5.0%; Nitrogen = 7.7%; Sulphur = 8.9%).

EXAMPLE 11.

In place of the 6.7 parts of 5-diethylsulphamyl-2-methoxyaniline used in Example 5 there are used 3.8 parts of *p*-nitroaniline. *p*-Dimethylaminobenzoylacet - 4-nitro - aniline crystallises from ethanol in the form of bright yellow needles which melt at 220—2° C.

EXAMPLE 12.

35 6 parts of *p*-N-dimethylaminobenzoylacet-4-nitro anilide are stirred with 45 parts of acetic acid and 5 parts of water, and the mixture is heated to the boil under a reflux condenser. 6 parts of iron filings are added in three portions during 10 minutes. The mixture is then stirred at the boil for 10 minutes, filtered and the filtrate is poured into 400 parts of water. The solid which separates out is filtered off, washed with water and dried. *p*-Dimethylaminobenzoylacet - 4 - amino-anilide crystallises from methanol in the form of buff-coloured prisms which melt at 169—170° C. On analysis the product is found to contain 67.6% of carbon, 6.4% of hydrogen and 13.6% of nitrogen. (Calculated for $C_{17}H_{19}O_2N_3$, Carbon = 68.6%; Hydrogen = 6.4%; Nitrogen = 14.1%).

EXAMPLE 13.

55 In place of the 6.4 parts of ethyl *p*-dimethylaminobenzoylacetate used in Example 1 there are used 7.6 parts of ethyl *p*-piperidino-benzoylacetate. *p*-Piperidinobenzoylacet-(2-N-methyl - N-octadecylamino - 5-carboxy)anilide crystallises from *n*-butanol in the form of white plates which melt at 155—7° C. On analysis the product is found to contain 74.2% of carbon, 9.5% of hydrogen and 6.1% of nitro-

gen. (Calculated for $C_{40}H_{51}O_4N_3$, Carbon = 74.3%; Hydrogen = 9.4%; Nitrogen = 6.5%).

65 The ethyl *p*-piperidinobenzoylacetate used in the above Example may be obtained by reacting *p*-piperidinobenzoyl chloride with ethylacetacetate and sodium ethoxide by the general method described by Claisen (Annalen 1986, Volume 291 at page 65) and hydrolysing the *p*-piperidinobenzoylacetooacetic ester so formed with an aqueous solution of ammonia and ammonium chloride at 35—40° C.

70 The *p*-piperidinobenzoyl chloride may be obtained by treating with thionyl chloride a toluene solution of *p*-piperidinobenzoic acid, which may be obtained by reacting N-phenyl-piperidine with phosgene and subsequently with sodium hydroxide.

EXAMPLE 14.

75 In place of the 6.4 parts of ethyl *p*-dimethylaminobenzoylacetate used in Example 1 there are used 10.1 parts of ethyl *p*-N-methyl-N-phenylaminobenzoylacetate and the chlorobenzene used as a solvent is replaced by xylene. *p*-N-Methyl - N-phenylaminobenzoylacet - (2-N-methyl - N-octadecylamino - 5-carboxy)anilide crystallises from acetone in the form of white needle-shaped crystals which melt at 137—139° C. On analysis the product is found to contain 74.9% of carbon, 8.7% of hydrogen and 6.3% of nitrogen. (Calculated for $C_{42}H_{50}O_4N_3$, Carbon = 75.3%; Hydrogen = 8.8%; Nitrogen = 6.3%).

80 The ethyl *p*-N-methyl - N-phenylaminobenzoylacetate used in the above Example may be obtained by reacting *p*-N-methyl-N-phenylaminobenzoyl chloride with ethylacetacetate and sodium ethoxide by the general method described by Claisen (Annalen 1896, Volume 291 at page 65) and hydrolysing the *p*-N-methyl - N-phenylaminobenzoylacetooacetic ester so formed with an aqueous solution of ammonia and ammonium chloride at 35—40° C.

85 The *p*-N-methyl - N-phenylaminobenzoyl chloride may be obtained by reacting a toluene solution of *p*-N-methyl-N-phenylaminobenzoic acid with thionyl chloride.

90 The *p*-N-methyl - N-phenylaminobenzoic acid (which has a melting point of 184—186° C.) may itself be obtained by reacting ethyl-*p*-N-methylaminobenzoate with iodobenzene in the presence of potassium carbonate and copper bronze, hydrolysing the product so obtained with a boiling 10% aqueous solution of potassium hydroxide, acidifying and crystallising the solid so obtained from ethanol.

EXAMPLE 15.

95 To a solution of 5.86 parts of *p*-N-benzyl-N-ethylaminobenzoylacet - (2-N-methyl - N-octadecylamino-5-carboxy)anilide in 100 parts of chloroform there is added a solution of 1.13 parts of sulphuryl chloride in 10 parts of chloroform. The resulting mixture is stirred

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for 15 hours at 20° C. and then the chloroform is evaporated off. The residue is crystallised from ethanol when *p*-N-benzyl-N-ethylamino-benzoyl- α -chloro-acet(2 - N-methyl - N-octadecylamino-5-carboxy)anilide is obtained having a melting point of 119—121° C. On analysis the product is found to contain 72.2% of carbon, 8.4% of hydrogen and 4.6% of chlorine. (Calculated for $C_{44}H_{62}O_4N_3Cl$, Carbon = 72.2%; Hydrogen = 8.5%; Chlorine = 4.9%).

EXAMPLE 16.

A mixture of 1.25 parts of *p*-N-dimethylamino-benzoylacet-4-aminoanilide, 1.5 parts of octadecenyl succinic anhydride and 5 parts of glacial acetic acid is heated for 30 minutes at 95—100° C. The mixture is cooled and the crystals which are formed are filtered off and washed with 2 parts of methanol. *p*-N-Dimethylamino-benzoylacet-4-(α -carboxy-methylen- α -octadecenyl - acetamido) - anilide crystallises from methanol in the form of white prisms, which melt at 139—142° C. On analysis the product is found to contain 71.5% of carbon, 8.8% of hydrogen and 6.2% of nitrogen. (Calculated for $C_{39}H_{57}O_5N_3$, Carbon = 72.2%; Hydrogen = 8.8%; Nitrogen = 6.5%).

EXAMPLE 17.

200 parts of a 5% methanolic solution of the sodium salt of *p*-N-benzyl-N-ethylamino-benzoylacet-(2-N-methyl - N-octadecylamino-5-carboxy)anilide (the colour coupler of Example 2) and 500 parts of a 7% aqueous solution of gelatine are added to 500 parts of a blue sensitive gelatino-silver halide emulsion which is stirred at 40° C. The emulsion so obtained is coated onto a paper base and the coated paper is dried. The photographic paper so obtained is exposed to blue light, developed in a colour developer containing 2-amino-5-diethylamino toluene, bleached and fixed when a bright yellow dyestuff image is obtained which has an absorption maximum at 430 millimicrons. This dyestuff image shows less absorption in the green region of the spectrum and has much better fastness to light than the dyestuff image which has an absorption maximum of 440 millimicrons, and which is obtained when the *p*-N-benzyl-N-ethylamino-benzoylacet-(2-N-methyl - N-octadecylamino-5-carboxy)anilide used in the above Example is replaced by 4-methoxybenzoylacet-(2-N-methyl-N-octadecylamino-5-carboxy)anilide.

PROVISIONAL SPECIFICATION

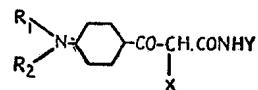
Substituted Benzoylacetanilides

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to new colour

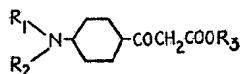
WHAT WE CLAIM IS:—

1. New colour couplers of the formula:—



where R_1 and R_2 are alkyl, aralkyl, aryl or cycloalkyl radicals, substituted or unsubstituted as hereinbefore defined, which can be the same or different or R_1 and R_2 are joined together to form with the nitrogen atom a heterocyclic ring, Y is an aryl radical, substituted or unsubstituted as hereinbefore defined, and X is a hydrogen or a chlorine atom.

2. Process for the manufacture of new colour couplers according to Claim 1, which do not contain an amino group in the aryl radical represented by Y which comprises heating an aromatic amine of the formula YNH_2 with an ester of the formula:—



where R_1 , R_2 and Y have the significance stated in Claim 1 and R_3 is an alkyl radical, and if desired subsequently replacing a hydrogen atom of the CH_2 group by chlorine by treatment with phosphorus pentachloride.

3. Process for the manufacture of new colour couplers according to Claim 1 which contain an amino group in the aryl radical represented by Y, which comprises treating a new colour coupler, as hereinbefore defined, containing a nitro group in the aryl radical represented by Y with a reducing agent.

4. Process for the manufacture of new colour couplers according to Claim 1 which contain an acylamino group in the aryl radical represented by Y, which comprises treating a new colour coupler, as hereinbefore defined, containing an amino group in the aryl radical represented by Y with an acylating agent.

5. A gelatino-silver halide emulsion containing a colour coupler as defined in Claim 1.

6. Process for the manufacture of new colour couplers as hereinbefore particularly described especially with reference to the foregoing Examples.

ALFRED O. BALL,
Agent for the Applicants.

couplers for colour photography.

The colour couplers conventionally used in colour photography for the formation of yellow image give azomethine dyestuffs with two main disadvantages. Firstly the dyestuffs are fugitive to light, especially the ultra-violet light

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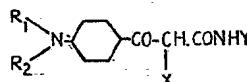
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present in normal daylight, so that the yellow coloured image fades on exposure to normal daylight, and secondly the dyestuffs have some undesired absorption in the green region of the spectrum.

We have now found that certain substituted benzoylacetanilides as hereinafter defined, have a very low absorption in the green region of the spectrum and have a marked absorption in the ultra-violet so that the excess unreacted colour coupler left in the photographic layer after colour development serves to absorb ultra-violet light and thereby largely protects the yellow azomethine dyestuff image from fading.

According to our invention we provide new colour couplers of the formula

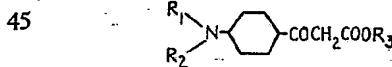


where R_1 is hydrogen, alkyl, aralkyl, aryl or cycloalkyl, R_2 is alkyl, aralkyl, aryl or cycloalkyl or where R_1 and R_2 are joined together to form with the nitrogen atom a heterocyclic ring, Y is an aryl radical and X is hydrogen or an atom or group replaceable in colour development.

The alkyl, aralkyl, aryl or cycloalkyl radicals may be substituted with for example halogen such as chlorine or bromine, alkyl groups such as methyl, ethyl, butyl, dodecyl or octadecyl, or alkoxy groups such as methoxy, or ethoxy, and the aryl radical may also be substituted with for example amino or substituted amino groups such as N-methyl-N-octadecylamino, or acid groups such as carboxylic or sulphonic acid groups.

As examples of atoms or groups represented by X which are replaceable during colour development there may be mentioned for example chlorine and bromine.

According to a further feature of our invention we provide a process for the manufacture of new colour couplers which comprises heating an aromatic amine of the formula YNH_2 , with an ester of the formula



where R_1 , R_2 , Y has the significance given above and R_3 is an alkyl radical, and subsequently replacing a hydrogen of the CH_2 group by chlorine or bromine if desired.

The radical R_3 may be for example methyl or ethyl.

The process of our invention may be conveniently carried out by heating the reagents together in a solvent which is inert under the conditions of the reaction for example xylene,

chlorobenzene or pyridine, and the product may be isolated by distilling off some or all of the solvent, cooling and filtering.

The esters used in the process of our invention may be made by condensing the appropriate p-substituted-aminobenzoyl chloride with alkyl acetoacetate and sodium alkoxide, hydrolysing the p-substituted-aminobenzoyl-acetoacetic ester so formed to the corresponding alkyl p-substituted-aminobenzoylacetate. The p-substituted-aminobenzoyl chloride may be made from the appropriate substituted aniline by treating it with phosgene, hydrolysing with caustic soda and separation of the carboxylic acid and then treating the carboxylic acid with thionyl chloride.

As examples of suitable esters for use in the process of our invention there may be mentioned ethyl or methyl p-dimethylamino-benzoylacetate, ethyl p-N-ethyl - N-benzyl-aminobenzoylacetate, ethyl p - piperidino-benzoylacetate, ethyl p-N-ethyl-N-cyclohexyl-benzoylacetate, ethyl p-N-methyl-N-phenyl-aminobenzoylacetate, and as examples of suitable aromatic amines there may be mentioned 3-amino-4 - N-methyl - N - octadecylamino-benzoic acid, sulphanilic acid, 3-amino-4-N-methyl-N-octadecylamino-benzene sulphonic acid, 3-amino - 4 - methoxy - benzene - sulphenyl-diethylamide, 3 - amino - 4 - chlorobenzotrifluoride, 2:5 - dimethoxyaniline, 4-amino - 4¹-chloro - diphenyl ether, o-toluidine, p-nitroaniline, o-amino-N: N-dimethylaniline or aniline.

The new colour couplers of our invention may be used in the developing solution or they may be included in a light-sensitive layer or in a non-light sensitive layer adjacent to a sensitive layer or separated therefrom by a water-permeable colloid layer.

It is a preferred feature of our invention, however, to include the new colour couplers of our invention in a light-sensitive gelatino-silver halide emulsion layer which forms part of a multilayer film or paper of the kind used for colour photography. For this purpose it is preferred to use those new colour couplers which contain a solubilising group and a substituent rendering them fast to diffusion, for example an alkyl chain containing at least 5 carbon atoms.

The multilayer film may be a natural order subtractively coloured negative in which the images are to be formed in colours complementary to the sensitives of the layers or one in which an unnatural order is used, for example, one in which in the top layer there is formed a yellow image of the blue parts of the object, in one of the two lower layers there is formed a cyan image of the green parts of the object and in the other, a magenta image of the red parts of the object.

The invention is illustrated but not limited by the following Examples in which the parts are by weight.

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EXAMPLE 1.

11 parts of 3-amino - 4-N-methyl - N-octadecylamino benzoic acid are dissolved in 70 parts of chlorobenzene and the solution is stirred and heated to 130° C. A solution of 6.4 parts of ethyl p-dimethylaminobenzoylacetate in 20 parts of chlorobenzene and 1 part of pyridine is added during 20 minutes. The solution is then heated and 27 parts of a mixture of ethanol and chlorobenzene are distilled off during 30 minutes. The mixture is boiled under a reflux condenser for 2 hours and a further 20 parts of chlorobenzene are then distilled off during 30 minutes. The reaction mixture is cooled and the anilide which crystallises out is filtered off, washed with 130 parts of boiling ethanol, and recrystallised from 175 parts of n-butanol. The product is obtained in the form of white needle-shaped crystals which melt at 159—161° C. On analysis the product is found to contain 73.1% of carbon, 9.2% of hydrogen and 7.1% of nitrogen. (Calculated for $C_{37}H_{57}O_4N_3$ Carbon = 73.2%; Hydrogen = 9.4%; Nitrogen = 6.9%). The ethyl p-

dimethylaminobenzoylacetate used in the above Example may be prepared by reacting p-dimethylaminobenzoyl chloride with ethyl acetacetate and sodium ethoxide by the general method described by Claisen (Annalen 1896, Volume 291, pages 65) and hydrolysing the p - dimethylaminobenzoylacetooacetic ester so formed with an aqueous solution of ammonia and ammonium chloride at 35—40° C. 25

EXAMPLE 2.

In place of the 6.4 parts of ethyl p - dimethylaminobenzoylacetate used in the above Example there are used 8.8 parts of ethyl p-N-benzyl-N-ethyl-aminobenzoylacetate. The p-N-benzyl - N-ethyl-aminobenzoylacet - (2-N-methyl-N-octadecylamino - 5-carboxy)anilide forms white needle-shaped crystals which melt at 125—127° C. On analysis the product is found to contain 75.3% of carbon, 9.0% of hydrogen and 6.0% of nitrogen (Calculated for $C_{44}H_{63}O_4N_3$ Carbon = 75.9%; Hydrogen = 9.0%; Nitrogen = 6.0%). 35

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